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Progress Report No. 7
July 1 to September 30, 1965

BUREAU OF MINES, PITTSBURGH, PA.

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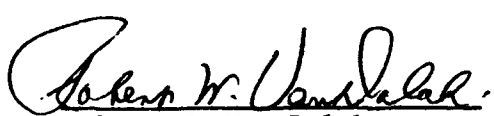
by

R. A. Van Meter
A. Strasser
E. L. Litchfield
J. Grumer

APPROVED:



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Research Director
Explosives Research Center

for
Space Nuclear Propulsion Office
Cleveland Extension
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INTRODUCTION

This is the seventh in a series of quarterly progress reports on hydrogen safety covering (a) review of existing practices, (b) delineation of areas in which new information needs to be developed, and (c) compilation of a safety manual based on fundamentals so as to be broadly applicable to operations involving hydrogen.

During the present reporting period, two hydrogen detectors were evaluated for performance; studies were continued of hydrogen plumes and the combustion characteristics of heterogeneous mixtures of hydrogen and air.

CURRENT PROGRESS

General Hydrogen Safety Studies (R. A. Van Meter, A. Strasser, S. R. Harris, and J. Grumer)

Three members of the staff visited SNPO-C headquarters in connection with designs of burn ponds for disposing large flows of hydrogen and for discussion of hydrogen safety manual preparation.

Members of the staff were consulted on hydrogen safety matters by representatives of other Federal agencies. One problem dealt with the planning of safety measures for structural fatigue testing of 6,000 gallon vessels filled with liquid hydrogen. An official of the British Ministry of Aviation, Safety Services Organization, also conferred with the staff on safety problems connected with the development of a new research laboratory that will include liquid hydrogen facilities.

Representatives of four makers of hydrogen detection equipment visited the Center or were otherwise in touch with staff members during the quarter regarding problems that have been encountered in the detection of hydrogen in air.

A staff member attended the Cryogenic Engineering Conference held August 23-25 at Rice University, Houston, Texas.

Hydrogen Plumes

In the previous report[1/] discussion of the literature on jets

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1/ Hydrogen Safety Progress Report No. 6, April 1 to June 30, 1965.

and plumes indicated the guidelines to follow in experimental and theoretical work on small-scale modeling experiments. The study of the formation and subsequent history of the plume resulting from a spill of liquid hydrogen or the escape of gaseous hydrogen will indicate criteria for optimum placement of detectors and the possible setting-up of quantity distance criteria. Furthermore, it may be possible to recommend conditions under which venting or flaring of waste hydrogen is more desirable.

Experimental work during the present quarter has been limited to exploratory experiments using helium rather than hydrogen. The safe handling facility for use with hydrogen studies has been designed but construction has been delayed. However, the problems of measurement of concentration, velocity and plume spread from a jet of helium are similar to those encountered in a jet of hydrogen.

One of the problems encountered in this study is the measurement of concentration fluctuations in a small volume. An optical method previously used by Rosensweig et al.[2/] to measure concentration fluctuations in a jet of smoky air discharged into ambient air has been adapted for the present study. The previous authors used a smoke developed by heating petroleum oil, a method which is undesirable for application to hydrogen studies. In the present work, we have used the smoke developed from the reaction between opposing hydrogen streams separately carrying acetic acid and cyclohexylamine. The smoke generator originally used employed liquid sprays; it could not be made to produce consistent amounts and concentrations of smoke. The generator has therefore been redesigned in light of this experience and expectations are that this difficulty has been overcome by the use of vapor laden streams of hydrogen or helium.

Further work on the optical probe method has indicated that in order to increase the response to small levels of light attenuation, the present miniature photovoltaic cell will have to be replaced by a photomultiplier type. The increased bulk of the latter necessitates the use of fiber optics to carry the light signal as well as the light source. The miniature cell could be inserted into the plume with minimum disturbance of the flow and thus require no "light pipe."

Measurement of plume velocity is being undertaken by a hot-wire anemometer. Since the response of this instrument depends not only on the velocity but the thermal conductivity of the gas, calibration has to be in terms of both velocity and concentration. The anemometer has been set up and calibrated for various helium-air concentrations. The determinations of velocities in a fluctuating helium plume require simultaneous concentration measurements which will be accomplished by the smoke technique.

2/ Rosensweig, R. E., H. C. Hottel, and G. C. Williams. Smoke Scattered Light Measurement of Turbulent Concentration Fluctuations. Chemical and Engineering Sciences, v. 15, 1961, pp. 111-129.

The problem of venting large flows of hydrogen gas may be approached by considering the theoretical basis of Morton's work on forced plumes.[3/] In considering the behavior of a forced plume from a source of finite size which delivers buoyancy, mass and momentum in a uniform environment, Morton points out that the plume fluid rises uniformly. One of the assumptions of Morton is a Gaussian profile of velocity, where the velocity at a point is proportional to $\exp(-k\, r^2/x^2)$, where x is the height above the source and r is the radial distance from the plume axis. The value of k determines the rate of decay of velocity and is subject to experimental determination.

Morton's approach for the forced plume indicates that as the vertical distance from the source increases, the velocity on the axis decreases at a slower rate than the plume radius increases. The latter increase is almost linear with distance. These trends are shown in figure 1, which is taken from Morton's paper. The result of these trends is that initially the Reynolds number increases with distance from the source, provided that the length parameter of the Reynolds number is based on the radius. However, the radius of the plume becomes ill-defined with distance and a decay constant k becomes important. This decay constant can be fairly large (of the order of 100), which would lead to an extremely rapid decay, leaving an effectively constant cross section for many diameters. Application of Morton's theory indicates that when the decay constant is large, the Reynolds number at about ten diameters downstream is about 60 percent of the original Reynolds number at the orifice. Since turbulent entrainment will thus also be large, the effect on the decision between flaring and venting will depend on the rapidity with which the lower limit of flammability is reached in the plume. Generally speaking, the sooner the lower limit is reached, the less need there is for flaring the output.

Hydrogen Detectors

Two hydrogen gas detectors were evaluated in experiments simulating likely operating conditions. Both units are console types sampling by diffusion and convection.

Unit HD-13

This console unit utilizes the principle of catalytic combustion and makes use of two filaments set up in two legs of a balanced Wheatstone bridge circuit. The diffusion head is provided with a test gas inlet port which permits remote in-place calibration.

As may be seen from figure 2, the detector head was found to be position sensitive. The meter readings were lower in the range of 0 to 1 percent hydrogen when the axis of the head was horizontal than when

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3/ Morton, B. R. Forced Plumes. Journal of Fluid Mechanics, v. 5, January 1959, pp. 151-163.

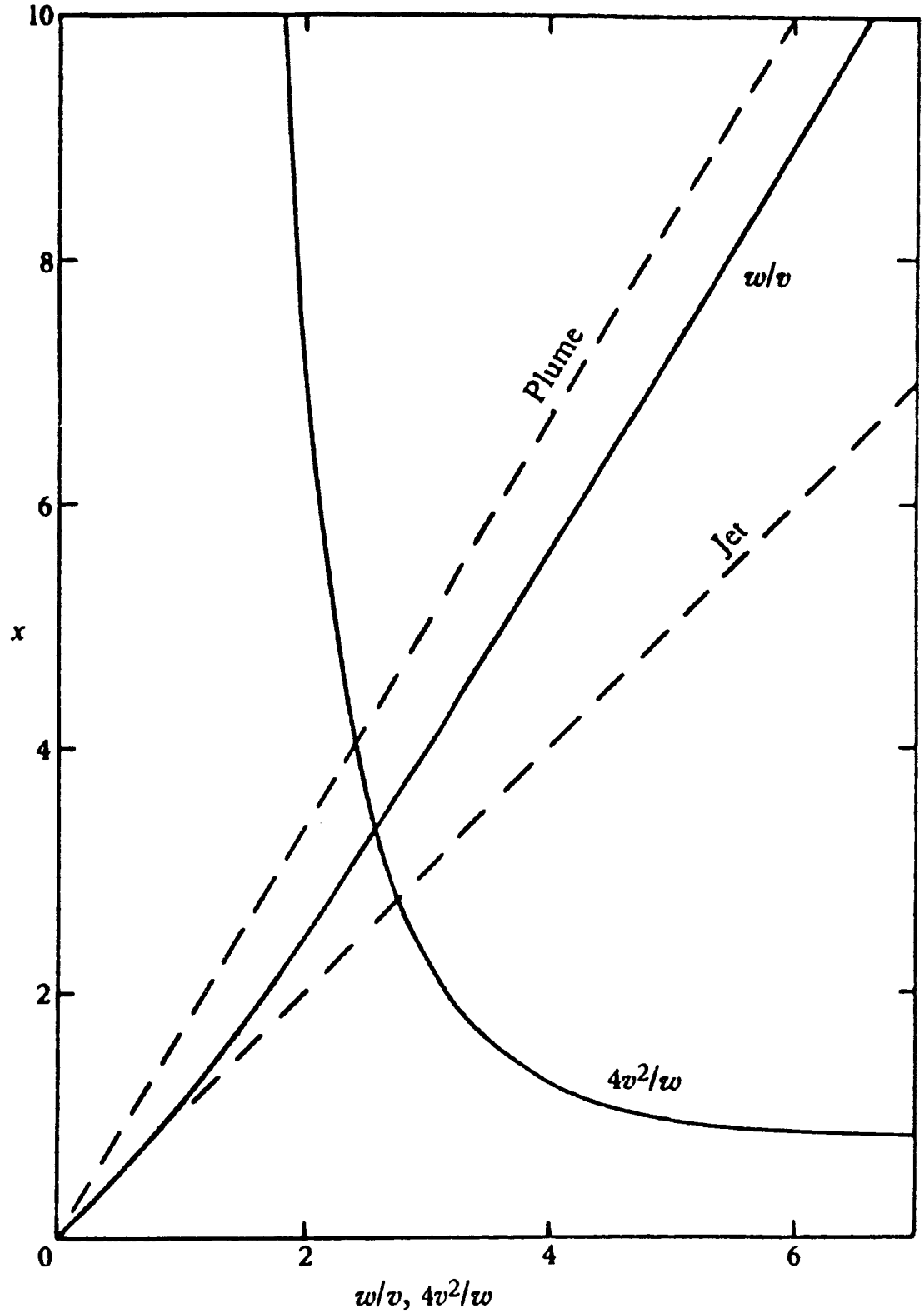

Figure 1. - The Behavior of a Forced Plume in a Uniform Environment. w/v is proportional to plume radius, v^2/w is proportional to velocity, x represents distance from a (virtual) source, dashed lines represent radii of pure plume and jet. (From Morton: J. Fluid Mechanics, January 1959, p. 155.)

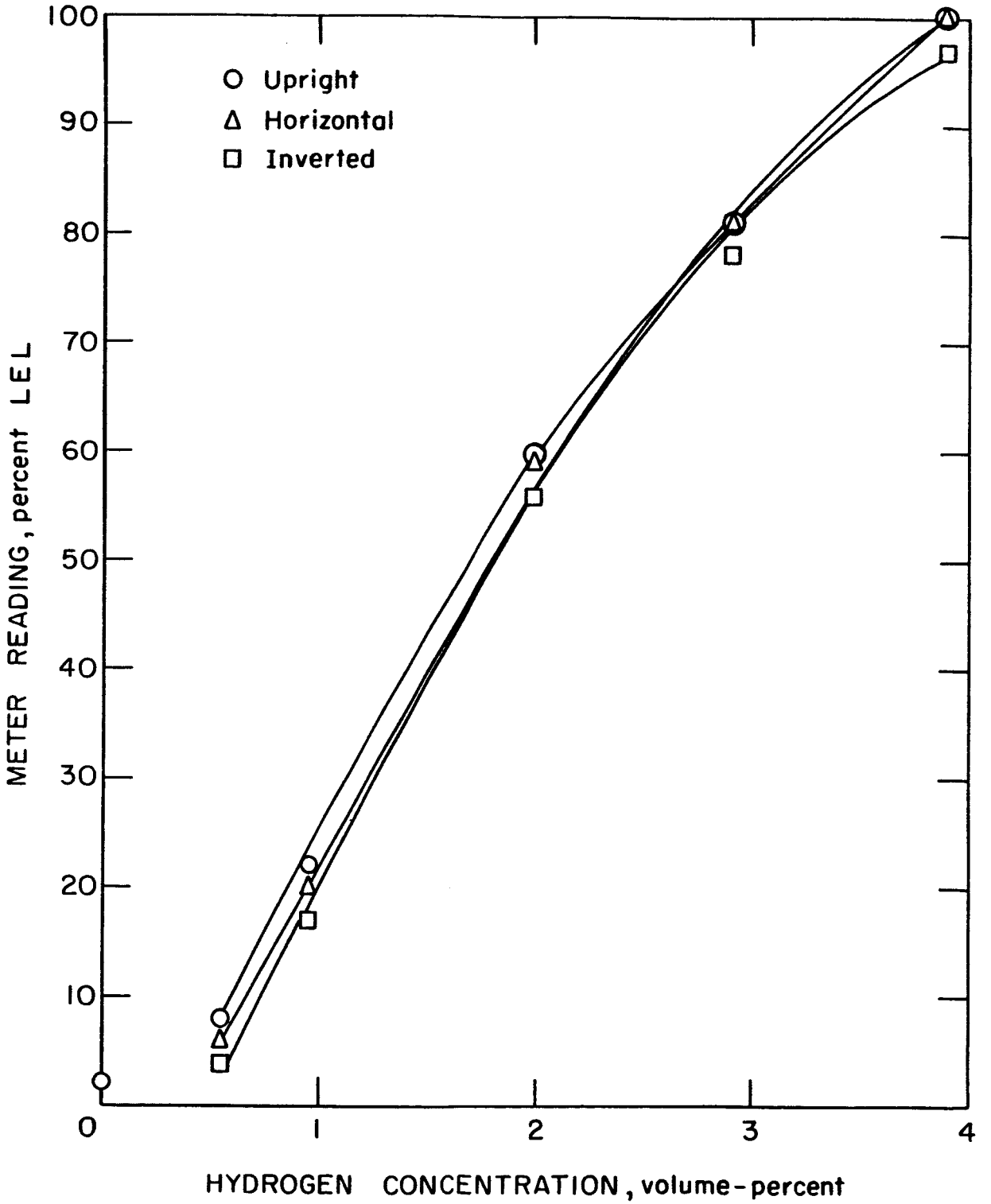

Figure 2. - Sensitivity of Unit HD-13 to Position of Detector Head.

the head was pointed straight up. At the 0.5 percent hydrogen level the difference was approximately 33 percent while at the 2.0 percent level the difference was 1.5 percent. The readings at the 3.0 and 4.0 percent hydrogen level were identical in either position. The readings, when the detector head was held in the inverted position, were lower at each concentration level.

Reproducibility of response to known concentrations of hydrogen is shown in figure 3. The largest range from the average of three trials at the same concentration was approximately 10 percent at the 0.5 percent hydrogen level. This difference decreased progressively with increasing concentration, vanishing at the 4.0 percent concentration level.

When the unit was at 50° C, higher readings were obtained than at room temperature. These findings are shown in figure 4. The change became progressively smaller as the concentration was increased. At 50° C the meter readings in the presence of 0.5, 1, 2, 3 and 4 percent hydrogen were respectively higher by 100, 22, 10, 6 and 4 percent of the meter reading at room temperature. These percent differences include the effect of a shift in the zero readings of 0.0 in air at room temperature to a reading at 50° C of 2.0 units. After this exposure to elevated temperature and cooling to room temperature, the zero reading remained at 2.0, the 0.5 percent hydrogen reading was 33 percent higher and the readings at 2, 3 and 4 percent hydrogen level were essentially the same as the original readings at room temperature.

Figure 5 illustrates the diminution of meter reading induced by subjecting the analyzer head to -24° C temperature. In the presence of 100 percent air the zero shifted significantly below that obtained at room temperature. After a 21 minute exposure of the analyzer head to progressively higher concentrations of hydrogen in air, up to 2.0 percent, there was no positive indication on the meter. At room temperature the meter indication for 2.0 percent hydrogen was 58. The meter indications at -24° C were 27 and 54, respectively, for hydrogen concentrations of 3 and 4 percent. The corresponding meter indications at room temperature were 80 and 98. On return to room temperature and prior to any manual adjustment, the instrument readings were higher by two to four units than those previously obtained at room temperature.

Unit HD-14

The remote head on this console type unit senses by diffusion and convection. This instrument is unique in that filament temperatures are determined photoelectrically; photocell output is calibrated in terms of the percent L.E.L. of combustible gas.

The first determination on this unit was of its response to 4.0 percent hydrogen in air. The average of six meter readings was 77.

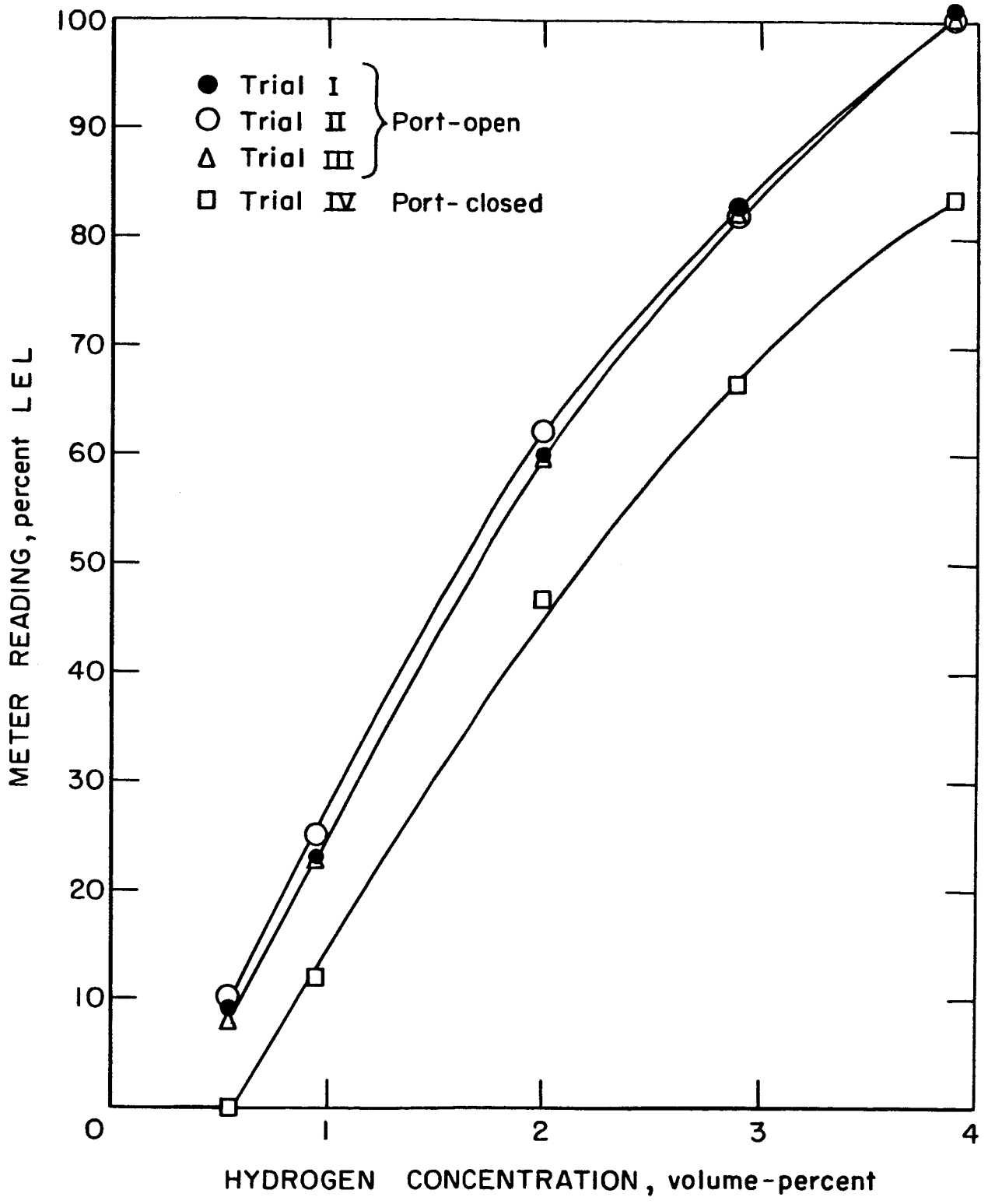

Figure 3. - Reproducibility of Response of Unit HD-13.

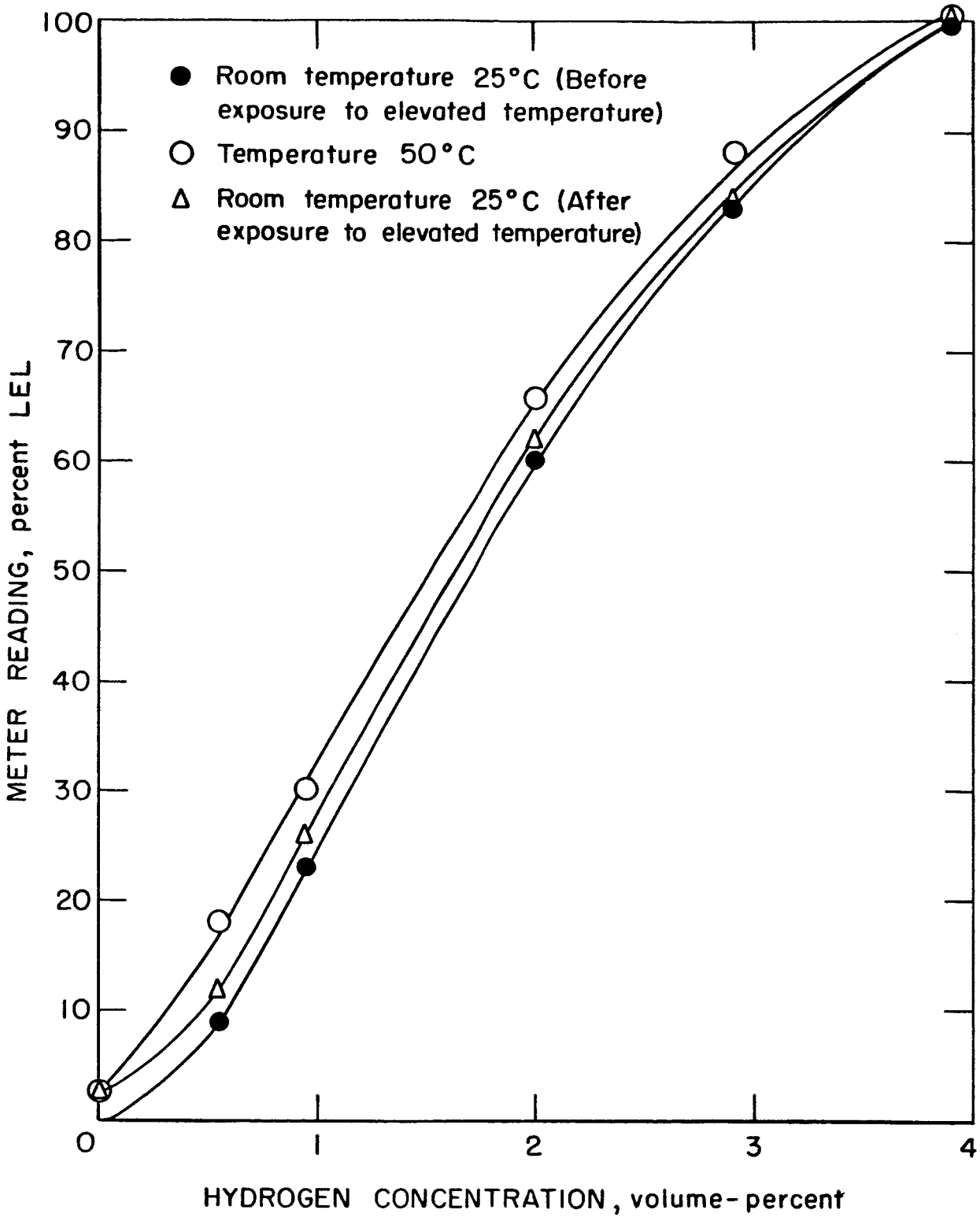

Figure 4. - Effect of Elevated Temperature on Unit HD-13.

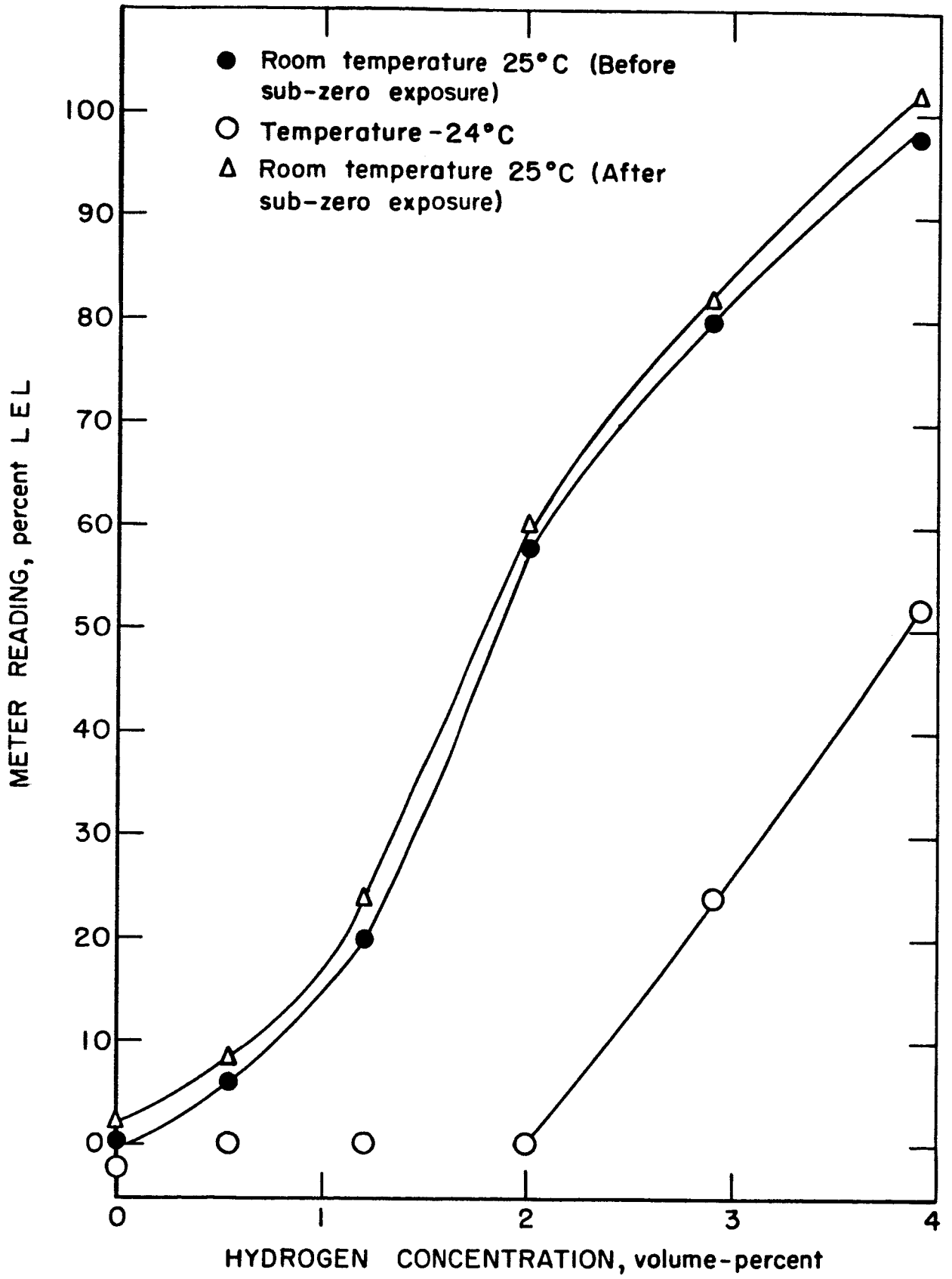

Figure 5. - Effect of Low Temperature on Unit HD-13.

When the detector was exposed to enough hydrogen to induce a reading of 100 on the meter, the required concentration of hydrogen was 5.3 percent.

Rate of response of meter to this concentration is indicated in figure 6. The average response time to reach 2/3 of the maximum reading for the 5.3 percent concentration was 23 seconds. The average recovery time to drop to 1/3 of the 100 percent reading was 60 seconds.

Figure 7 shows the results obtained when the detector was checked for reproducibility of response to various known concentrations of hydrogen in air. The instrument did not respond to a concentration of 0.5 percent hydrogen. In three trials with 1 percent hydrogen, the maximum spread from the average meter reading was 20 percent. This percentage deviation became progressively smaller with increase in hydrogen concentration. The differences were 4.6 percent of the meter reading with 2 percent hydrogen and 1.3 percent with 4 percent hydrogen.

No hazard was detected of ignition occurring within the detector head and flame passing through the flame arrestors. The head was placed in the test chamber and subjected to increasing concentrations of hydrogen in air up to 100 percent. The hydrogen concentration was then gradually decreased by addition of air to zero percent hydrogen. This procedure resulted in approaching and passing through the stoichiometric concentration from fuel lean and fuel rich mixtures.

As may be seen from figure 8, the instrument no longer functioned as it did prior to the exposure to 100 percent hydrogen. The meter reading for 1.0 percent hydrogen in air was formerly 12 and was 77 for 4.0 percent hydrogen; after this exposure the instrument no longer responded to 1.0 percent hydrogen in air and read 55 on the meter for 4.0 percent hydrogen in air.

There was a further diminution of meter reading when the detector head was exposed to various concentrations of hydrogen in air at 50° C. The resulting data are in figure 9. Compared to a meter reading of 12 for 1 percent hydrogen at room temperature, the instrument gave no positive meter indication in the presence of 2.0 percent hydrogen at 50° C. In the presence of 4.0 percent hydrogen in air, the meter indication was 40 at 50° C compared to 55 at room temperature. The room temperature readings were taken immediately prior to the determinations at 50° C.

When the detector was exposed to mixtures of hydrogen in air which had been bubbled through water, there was a decrease in meter reading below the zero setting. This negative reading became larger as the concentration of hydrogen in air was increased to 4.0 percent, with a corresponding increase in water concentration.

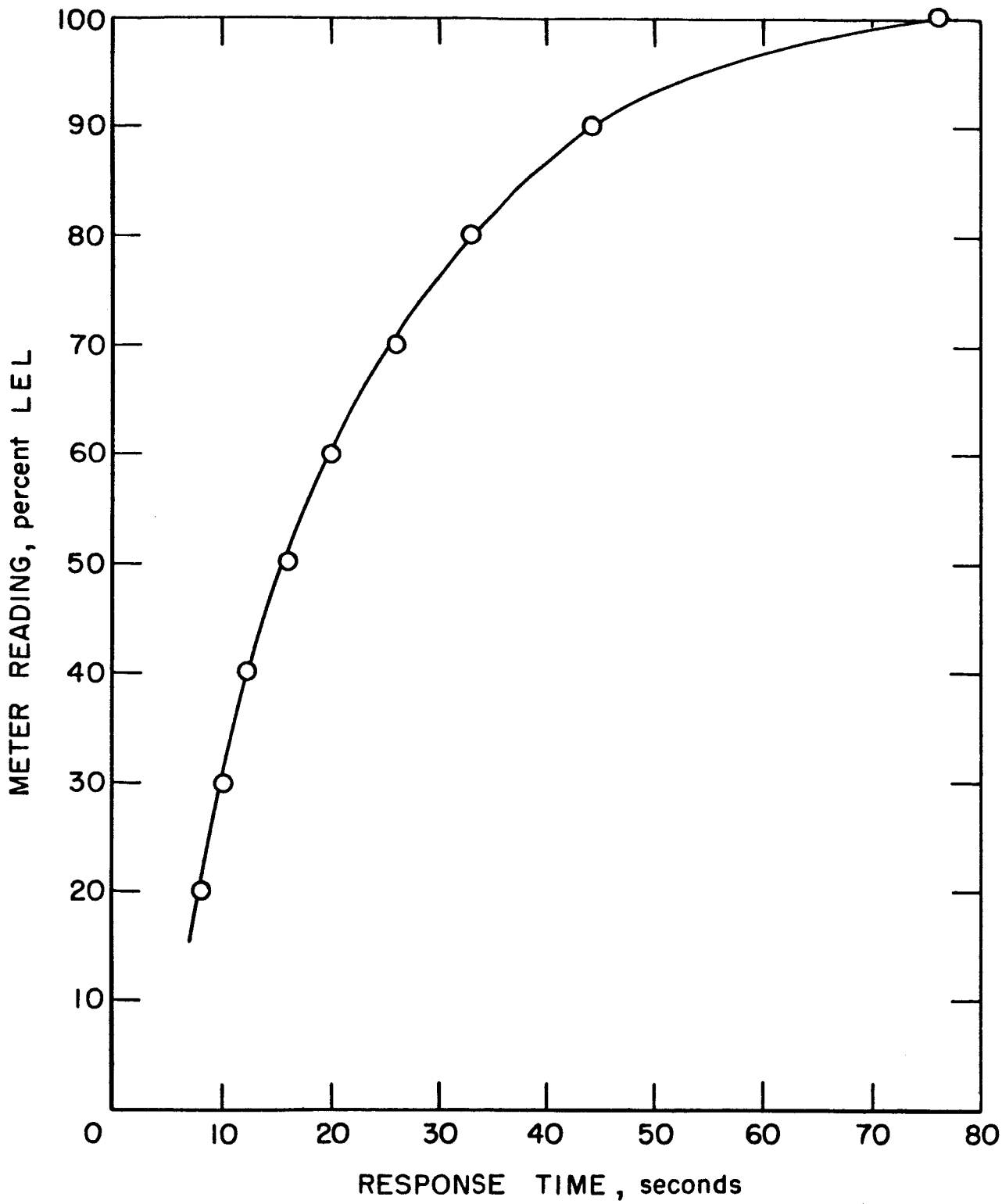

Figure 6. - Response Time of Unit HD-14 to 5.3 Percent Hydrogen.

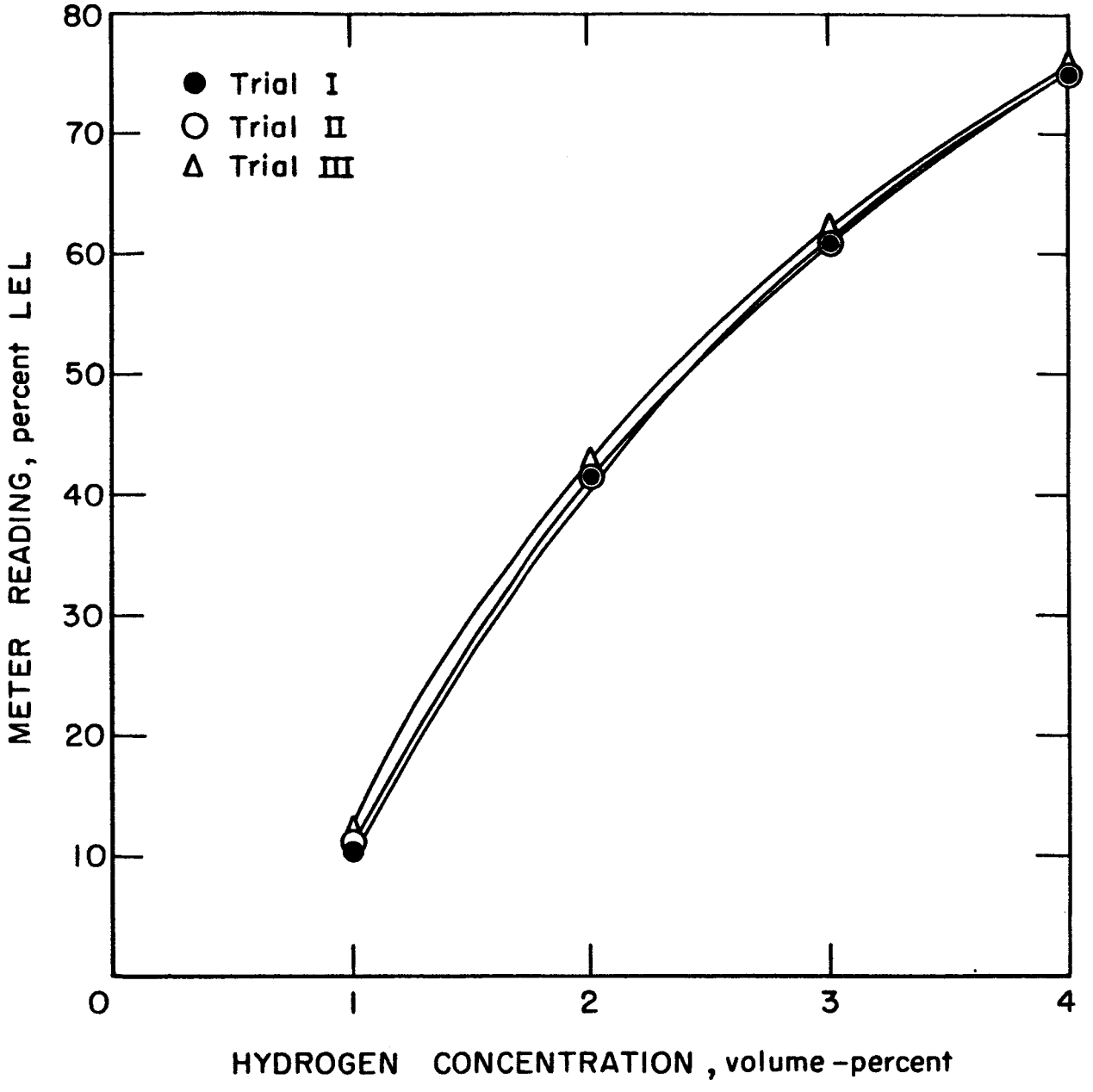

Figure 7. - Reproducibility of Response of Unit HD-14.

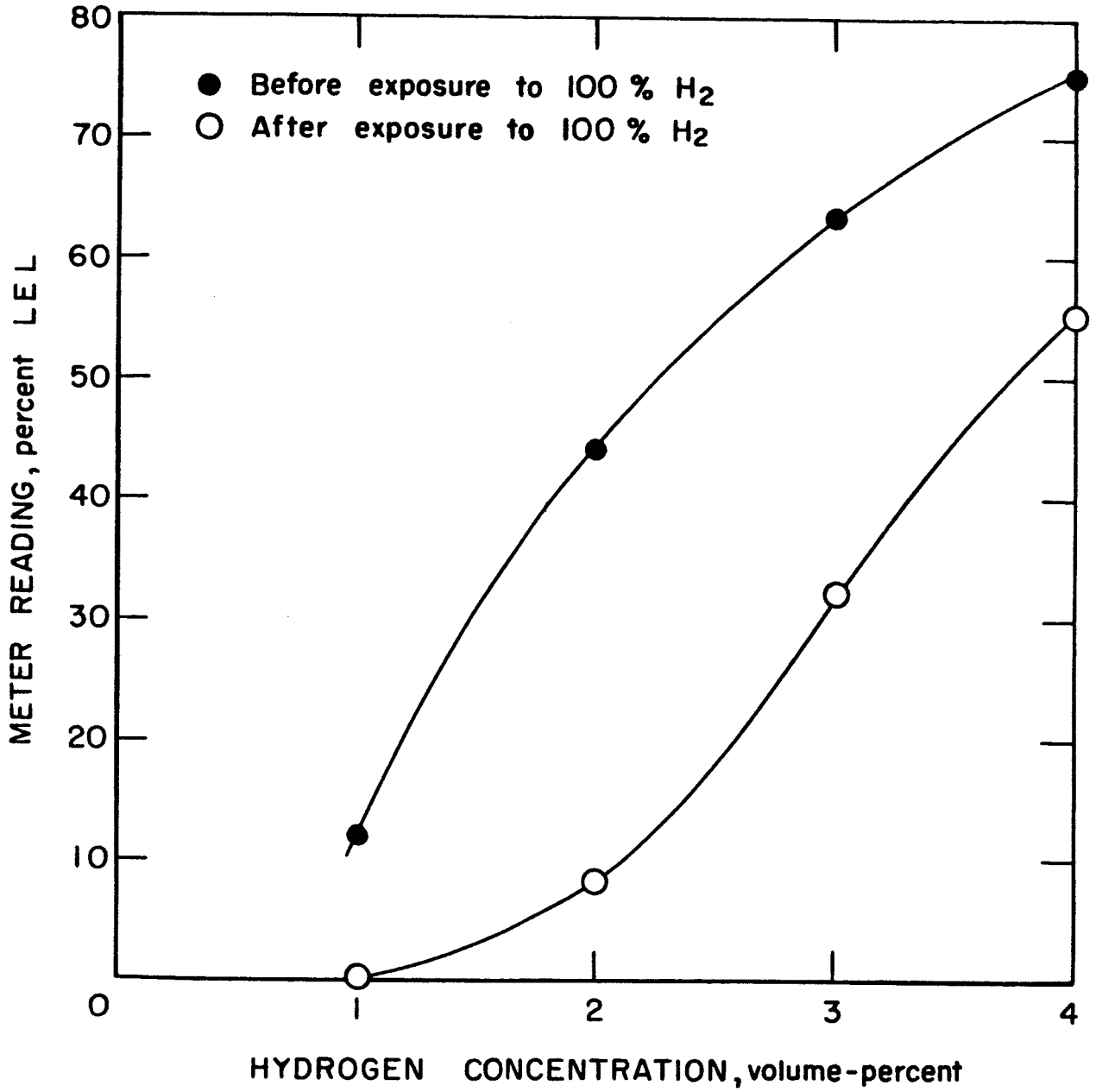

Figure 8. - Effect of Exposure to Pure Hydrogen of Unit HD-14.

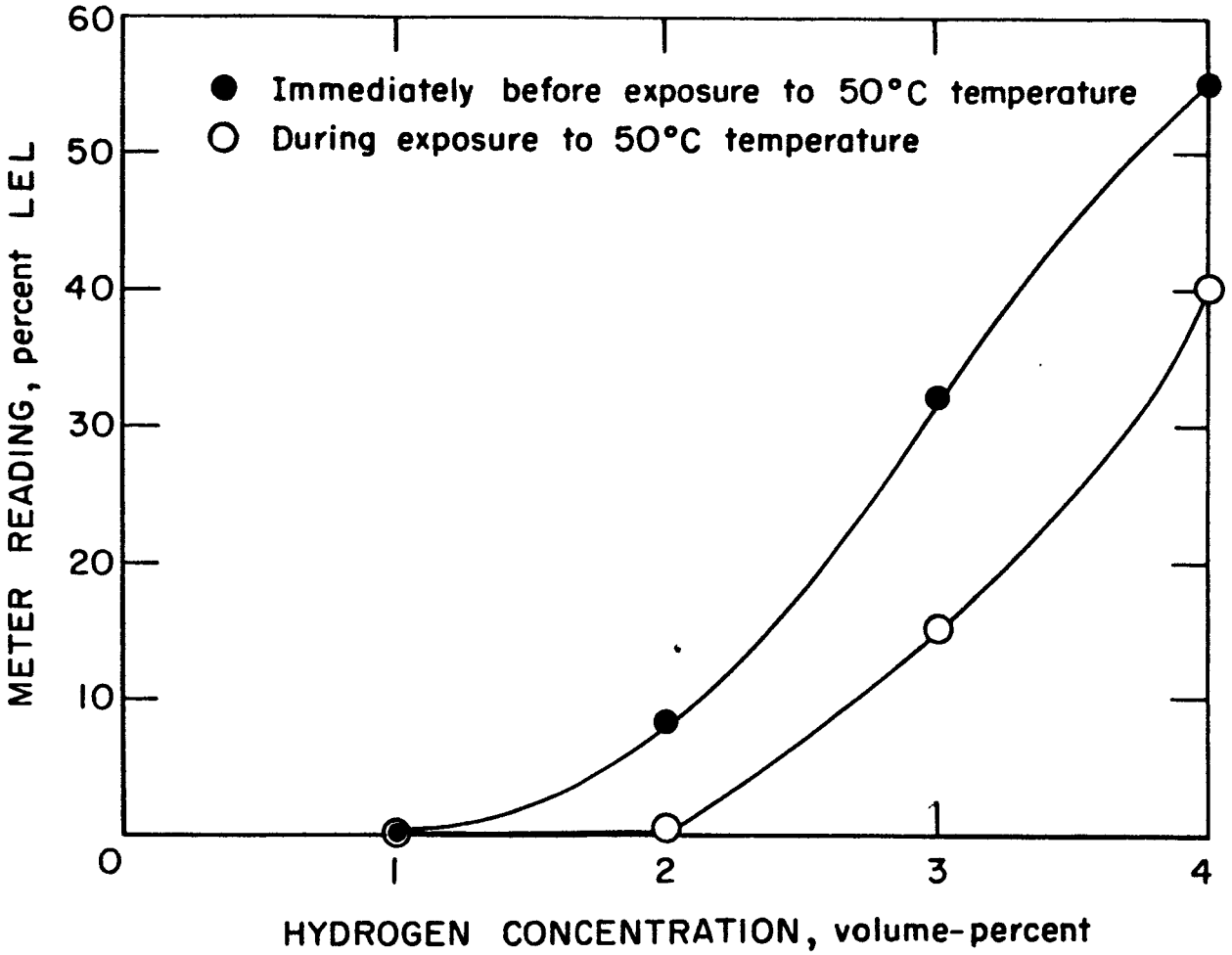

Figure 9. - Effect of Elevated Temperatures on Unit HD-14.

Hydrogen Explosion Hazards (J. N. Murphy and E. L. Litchfield)

The combustion characteristics of incompletely mixed hydrogen and air mixtures (gradient mixtures), were compared with those of incompletely mixed hydrogen and oxygen mixtures. Both experiments were conducted in the 24 × 24 × 2.25 inch two dimensional chamber described previously (Hydrogen Safety Progress Report No. 5, January 1 to March 31, 1965). The gases were ignited with an electric spark at the planes where the desired composition existed; the combustion wave was followed along the diagonals of this 24 inch square plane of the chamber.

In non-homogeneous mixtures of hydrogen and oxygen, as prepared by the diffusion technique, the maximum flame velocities observed were about 6,200 ft/sec (1.9 mm/μsec) in the hydrogen rich end of the chamber and 2,300 ft/sec (0.7 mm/μsec) in the oxygen rich end of the chamber when the mixture was ignited at the 32 percent hydrogen-68 percent oxygen composition plane. Ignition at other composition planes yielded flame velocities on the order of 2,900 ft/sec to 4,800 ft/sec, but in all cases the velocities were higher than observed with homogeneous mixtures. In the very early portion of the combustion, the pressures at the chamber walls rose at about 1.5 psi/μsec to maximum values of 50 to 60 psig, which were about 50 percent of the later peak combustion pressure. Velocities and maximum rates of pressure rise obtained so far with gradient hydrogen-air mixtures were each about three orders of magnitude below those of gradient hydrogen-oxygen mixtures. Velocities of the former mixtures were in the range of 10 ft/sec; maximum pressure rise rates were about 5 psi/msec. Oscillations were observed in the initial phase of the pressure waveform when 100 percent oxygen was used, but were negligible when air was used. This series will include studies of the effects of other nitrogen-oxygen ratios.

Int--BuMines,Pgh.,Pa.